INFLUENCE OF THE WATER-GAS-SHIFT REACTION ON LOW TEMPERATURE PRETREATMENT OF SUBBITUMINOUS COAL

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Abstract
In previous studies, we showed that subbituminous coals treated with CO and water in the presence of a base (NaOH, Na_2CO_3) at mild temperatures (300 °C) produced an improved liquefaction feed material. In this reaction coal undergoes significant structural modification as observed by the increased THF and pyridine solubility, lower oxygen content and higher atomic H/C ratio relative to the raw coal. In this paper, we discuss the impact of the water-gas-shift (WGS) reaction on the coal reaction. Strong correlations were found over a wide range of reaction conditions between THF solubility of the pretreated coal and both CO conversion and amount of hydrogen consumed. The effect of various sodium and ammonium salts on the reaction is discussed.

Introduction
Fischer and Schrader,[1] pioneered the liquefaction of coal with CO and water. Appell and Wender[2] in the late 60's revived interest in this approach as an alternative method for directly producing hydrogen in the liquefaction reactor. This led to the CoSteam process for liquefying low rank coals. Since then, the application of CO and water for liquefying various materials and the effect of added catalysts on these reactions have been widely studied.[3] The addition of a strong base to this system significantly improves the conversion of coal to liquid products.[4] In recent years, CO and water has been used to treat coal to enhancing its conversion during liquefaction and improve the product mix.[5,6] This treatment results in chemically and structurally modifying the coal to produce an improved feed material.

The chemistry of the WGS reaction and the intermediates involved in the reaction are complex. Various mechanisms and intermediates have been proposed for coal conversion using CO and water.[7,8] Recently, Horvath et al.[9] provided evidence for the formation of formate ion at liquefaction temperature when they reacted coal with CO and water at 400 °C in a specially fitted ^{13}C NMR spectrometer. At significantly lower temperatures (200 °C and below), King et al.[10] showed that CO reacts rapidly with KOH to quantitatively form potassium formate. They showed that the production of hydrogen from the WGS reaction at these temperatures is catalyzed by the addition of a catalyst precursor such as $Mo(CO)_6$. In the absence of a suitable catalyst, the formate ion is relatively stable up to 300 °C.[11] Above 300 °C formate decomposes mainly to CO_2 and H_2 and partially undergoes dehydration to form CO. From the literature,[2,4,7] it is evident that the success of liquefaction with CO and water has been attributed to the intervention of the formate ion. In this paper we present results to show the effect of the WGS reaction on the reaction of coal with CO and water at rather mild temperatures at or below 320°C.

Experimental
Coals - Wyodak coal from the Black Thunder (BT) mine in Wright, Wyoming, was ground to -200 mesh, riffled and stored in tightly sealed containers. Ultimate analyses was as follows: carbon, 73.9%; hydrogen, 5.2%; nitrogen, 1.3%; sulfur, 0.6%; oxygen, 19.0%O (by difference). Ash content on a dry basis was 6.12 wt%. All results are expressed as weight percent, moisture and ash-free coal (maf).
Reaction Conditions - Experiments were conducted in a 25 ml micro-reactor by adding, per gram of maf coal, up to 3 g of water and 0.06 to 1.0 mmol of promoter salt (NaOH, Na_2CO_3, NaCl, NH_4NO_3). The reactor was pressurized with CO (300-800 psig) and heated to 250 to 320°C a fluidized sandbath. The reactor was agitated at a rate of 400 cycles/min for periods between 30 min to two hours, and then rapidly quenched to room temperature. Gaseous products were collected and analyzed by gas chromatography. Solid and liquid products were recovered from the reactor using distilled water, filtered, and dried. Water-insoluble materials were separated by extracting with THF in a Soxhlet thimble for 18 hours and drying overnight at 80 °C at 16 kPa. The THF solubles were concentrated by removing excess THF. A 50:1 excess volume of pentane was added and the pentane insoluble material was filtered and dried. Only a very small amount of pentane soluble material was recovered which represented only a small proportion of the overall products, particularly when high CO pressures

were used.[6] In coal reactions with a promoter and in the absence of CO or at low CO pressures (400 psig and below), soluble humic acids were recovered from the aqueous phase by precipitating the colloidal material with HCl (pH 1-2) followed by centrifugation and drying. The acidified aqueous layer was further extracted with ether. Total mass recovery, on a maf basis, was typically 90% or better at or below 300 °C and between 80-85% at 320°C. THF solubility of the solid products after pretreatment is defined as the proportion of material soluble in THF plus any humic acids, if present.

Results and Discussion

Water-Gas-Shift Reaction. Total CO_x recoveries from coal treatment runs with CO were typically greater than 98% and included unreacted CO, gaseous and dissolved CO_2, and formate ion present in the aqueous phase. For those reactions to which NaOH was added, the concentration of dissolved formate, which was based upon the equivalents of Na present, accounted for 4% of the total CO feed. No correction was made when any of the other salts were used in these reactions. Dissolved CO_2 in the aqueous phase, calculated at ambient temperature following Henry's law, accounted for only 1% of the total CO feed. CO conversions increased with temperature, with the maximum conversion of 34% being observed at 350 °C, which was equivalent to conversion of 7.5 mmol of CO per gram maf coal feed.

For a 20% conversion of CO, the theoretical amount of hydrogen produced from that portion of the CO that was converted to CO_2 via the WGS reaction was equivalent to 4.5 mmol/g maf coal. Addition of a promoter increases CO conversion significantly, but these values are low relative to the thermodynamic equilibrium value. Recovery efficiencies of H_2 were quantitative when coal was absent but decreased sharply in the presence of coal. The missing H_2 presumably was incorporated into the treated product and is reported as H_2 consumption in mg H_2/g maf coal.

Conversions of CO in aqueous solutions containing up to 2 mmol NaOH per 45 mmol CO were determined over a temperature range from 250 to 350 °C for a one hour reaction period (see Table 1). In the absence of NaOH, only 1% of the CO is converted. In the presence of NaOH, conversions increased steadily with temperature. Doubling the reaction time from one hour to 2 hours increased conversion by about 25% at 300 °C. However, under no circumstances were CO conversions equal to those that were reported previously for similar reaction conditions (~ 80%) attained in this study.[8]

In the presence of coal at 300 °C, 10% CO was converted in 1 hour (see Table 2). This level of conversion was significantly greater than the 1% observed in the absence of coal. When both NaOH and coal were present, 20% of the CO was converted which equalled that observed in aqueous NaOH in the absence of coal. The increase observed with coal, but in the absence of base, suggests that the cationic component in the coal may be acting as a weak promoter. This increase is still much less than observed with added NaOH, since coal added to caustic solution gave no additional CO conversion. The data indicate that reaction time is a strong dependent variable for converting CO. Conversion progressively increased over a period from 30 to 90 min from 12 to 23%, as shown in Table 3. Other salts also promote the WGS reaction. CO conversions in the presence of coal at 300 °C with added sodium carbonate, bicarbonate and chloride were 17, 21 and 16%, respectively. Since CO conversion occurs equally well in the presence of sodium chloride, obviously a basic system is not necessary for initiating CO conversion. Ammonium nitrate appears not to be a significant promoter for CO conversion, possibly because it decomposes at approximately 250 °C.

Coal Reaction. Treating Wyodak coal in CO/NaOH/water at 300 °C results in a 8 to 13 wt% decrease in the amount of solid material, as shown in Table 3. In the absence of CO or at lower CO pressures, a small amount of humic acids are also found in addition to a trace of ether soluble material. Only trace quantities of hydrocarbon gases are produced during the treatment. The major part of the decrease in weight is due to elimination of water and carbon oxides. The sizable increase in THF solubility of the treated material both in THF and pyridine indicates that significant modification has occurred to the coal structure. The solubility behavior of this THF material indicates it is almost completely pentane insoluble. Although the presence of NaOH is not necessary for achieving a reasonably high THF solubility in the water-insoluble product, there is improvement when it is present. However, the absence of CO has a much more dramatic affect on the reaction. The solubility in THF of the water-insoluble material obtained from hydrothermally treating the coal at 320°C in the absence of CO was only 11%. The water-insoluble material from the hydrothermal treatment in the presence of added NaOH at 320 °C was 9% soluble in THF. In the case of the NaOH

treatment 4 wt% humic acids and 1 wt% ether solubles were formed.

The amount of hydrogen that could not be accounted for in the material balances from these various CO treatments is presumably consumed by the water-insoluble product. The amount increased with increasing reaction time as well as temperature. For reaction periods from 30 to 90 min, the level of hydrogen incorporation in the product ranged from approximately 0.4 wt% up to 0.7 wt%, which is consistent with increases reported previously.[5]

Other salts also promote the conversion of CO, as well as produces a water-insoluble material having increased THF solubilities, as shown in Table 2. The THF solubilities of the water-insoluble materials from the sodium carbonate, bicarbonate and chloride promoted reactions were similar in magnitude to the amount of THF soluble material obtained when using NaOH. Ammonium nitrate, however, gave a material that was only 10% soluble. It is not entirely clear why NH_4NO_3 should give a lower THF solubility, even though it decomposes above 200 °C (m.p. 172°C). The hydrothermal reaction with CO should still result in a sizable improvement in the THF solubility of the water-insoluble product.

At high CO pressures, the total amount of coal derived material that is soluble in THF is equal to the THF solubility of the water-insoluble product. In the absence of CO or at low CO pressures, however, the total amount of THF soluble material derived from the coal includes humic acids and ether soluble material. A plot of total THF solubles versus the amount of converted CO from both current, as well as previously reported results, is shown in Figure 1. In these runs, Wyodak coal was treated at different temperatures, at different CO pressures, with different amount of water, and with different salts at different salt concentrations. The plot indicates a strong correlation exists between these variables.

A plot of THF solubility versus H_2 consumption also shows a strong correlation with an apparent intercept that approaches the origin (Figure 2). This parallel between THF solubility and H_2 consumption and the close approach of the H_2 intercept to the origin indicates that addition of hydrogen during treatment of the coal must be highly efficient.

Conclusions. The presence of sodium hydroxide, carbonate, bicarbonate and chloride salts promotes the conversion of CO at temperatures between 250 and 350 °C. Coal also promotes CO conversion but to a lesser extent than the sodium salts. The addition of Wyodak coal to these systems results in a water-insoluble material that is significantly more soluble in THF. Correlations were found between both the level of CO conversion and H_2 consumption and the THF solubility of the water-insoluble product. The close approach of both of these correlations to the origin is an indication of the high H_2 utilization efficiency of this treatment reaction.

Acknowledgement

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Table 1. Effect of Temperature on the WGS Reaction								
Temperature, °C	350	320	320	300	300	300	250	250
CO press, psig	800	800	800	800	800	800	800	800
NaOH Conc, mmols/g maf coal	1	1	Nil	1	1	Nil	1	Nil
Reaction Time, min	60	60	60	120	60	60	60	60
CO_x recovery, mole%	102	100	100	91	96	97	97	98
CO Conv, mol%	34	27	1	19	15	1	5	1

Table 2. Effect of Promoter Salt on Treatment of Wyodak Coal[a]						
Salt promoter	none	NaOH	Na_2CO_3	$NaHCO_3$	NaCl	NH_4NO_3
Salt conc, mmol/g maf coal	-	1	0.5	1	1	1
CO_x recovery, mol%	97	100	99	101	97	99
CO Conv, mol%	10	20	17	21	16	13
CO Conv, mmol/g maf coal	2.0	4.0	3.4	4.0	3.0	2.2
Missing H_2, % theoretical	84	86	82	86	51	42
H_2 Consumption, wt% maf coal	0.33	0.63	0.56	0.60	0.31	0.18
WI[b] Product, wt% maf coal	90	92	93	89	90	88
Solubility of WI in THF, wt%	22	28	32	24	24	10

a. 300 °C, 800 psig CO cold (approx. 20 mmol/g maf coal), 3 g water/g maf coal.
b. WI = water insoluble product

Table 3. Effect of Treatment Time[a]			
Reaction Time, min	30	60	90
CO_x recovery, mol%	98	100	100
CO Conv, mol%	12	20	23
CO Converted, mmol/g maf coal	2.4	4.0	4.0
Missing H_2, % theoretical	70	86	84
H_2 Consumption, wt% maf coal	0.33	0.63	0.68
WI[b] Product, wt% maf coal	91	92	87
Solubility of WI in THF, wt%	20	28	26

a. 300 °C, 800 psig CO cold (approx. 20 mmol /g maf coal), 1 mmol NaOH/g maf coal, 3 g water/g maf coal
b. WI = water insoluble product

	Table 4. Legend for Figures 1 and 2[a]				
	Promoter Salt	mmol Salt/ g maf coal	CO Pressure, psig	Temp °C	Reaction Time, min
A	NaOH	0.06	300	250	60
B	NaOH	0.5	550	275	60
C	NaOH	0.06	800	250	60
D	NaOH	1.0	800	300	60
E	NaOH	1.0	800	300	30
F	NaOH	1.0	800	300	90
G	NaOH	1.0	800	320	60
H	Na_2CO_3	0.5	800	300	60
I	$NaHCO_3$	1.0	800	300	60
J	NaCl	1.0	800	300	60
K	NH_4NO_3	1.0	800	300	60

a. Water added at 3 g/g maf coal.

Fig.1 The Effect of CO conversion on THF
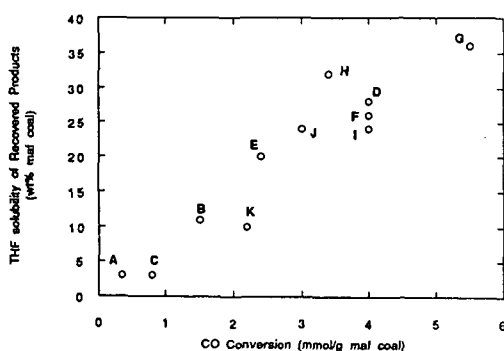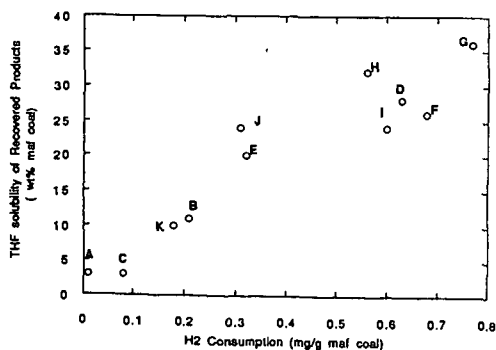Solubility of Treated Coal

Fig.2 The Effect of Hydrogen Consumption on THF
Solubility of Treated Coal

THE PERFORMANCE OF BIOMASS DERIVED ULTRACARBOFLUIDS IN STANDARD DIESEL ENGINES

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Keywords: Bio-ultracarbofluids, Diesel fuel replacement.

Introduction

The impetus for the replacement of petroleum-derived diesel fuels ,whether wholly or partially,arises from the need to conserve a non-renewable energy resource and because of the significant pollutants generated by their combustion.However the use of bio-mass derived fuels may also offer strategic and economic advantages.

The majority of the world's energy resources occur in nature as solids e.g coal and various biomass and waste materials.Bio-fuels such as wood ,charcoal and agricultural residues are a major source of energy in many of the developing countries providing as much as 14% of the current world energy requirements.This is eqivalent to some 25 million barrels of oil a day,the same as OPEC's current production[1].Worldwide there is substantial land potentially available for growing energy crops.

The possibilities for diesel fuel replacement are;
  i   Complete replacement by a suitable vegetable oil e.g. rape seed oil [2] , soya bean oil [3], esterified sugar beet exract [4].Some research is also in progress into the use of elephant grass oil (Miscanthus)[5].
  ii Partial replacement by blending diesel with vegetable oils in varying proportions up to 20% by weight[6].
  iii Partial replacement by blending with an aqueous suspension of a non-renewable fossil fuel e.g.coal[7].
  iv Complete replacement by a slurry of coal in vegetable oil.
  or
  v   Complete replacement by a 100% bio-renewable ultracarbofluid. This could comprise some formulation of water, charcoal , and a vegetable derived oil.

The research summarised here is concerned with the last alternative.

Biomass-Derived Ultracarbofluids

Typically biomass derived ultracarbofluids consist of charcoal 45%-54%,oil-blend 16%-29%, water 30%-35%, surfactant 1%, plus corrosion inhibitors etc in trace amounts.

The solid constituent is of necessity finely-divided and in practice needs to be ground to < 20µm particles in order to minimise erosion in the fuel system i.e transfer lines and injectors.Clearly low ash charcoal is preferable for optimum energy efficiency but also mainly to keep residue build-up in the engine to a minimum.The higher the proportion of charcoal in the blend the greater the gross energy output.

The possible replacement of the fuel oil fraction ,typically 15% to 30%,by a bio-renewable vegetable oil is of considerable interest.Several commercially available oils have been tested as fuel components.Using ordinary vegetable oils as fuel usually results in problems with severe engine deposits,ring sticking ,accumulation of deposits on injector nozzles and lubricant contamination ..For this reason vegetable oils for use as fuel or fuel component have to be modified by trans-esterification. Rapeseed methyl ester shows great potential for use as fuel or as a fuel component for diesel engines.

The ultimate test for any fuel is to determine how well it burns over long periods of time, and the impact of its use on the combustion system and auxilliary equipment.However any blend can, of course, be characterised by conventional property measurements i.e viscosity,cetane number,grossheat combustion , cloud point, flash point, density, particle size and ash content.

Ucf Peformance

Coal-water slurries have been studied extensively as fuels.Initial results confirmed that the main problems encountered when using coal-water slurries are,with fuel injection system operability, wear and poor combustion efficiency of the coal particles .

However, improvements have been recently been reported in reduced wear of injection components,by the addition of lubricant [8].

Bio-ultracarbofluids

Initial research on bio-ultracarbofluids utilised a 4-stroke single cylinder,indirect injection diesel engine with speed range of 650-800 rpm . The optimum perfomance has been achieved using coal 40%,water 30%, fuel oil 29%, additive 1%. The operating variables were;

-coal particle mean diameter :   8 μm

-injection timing :   42 degrees BTDC

-injection pressure :   12.5 MPa

-intake air temperature :   313 K

-intake air pressure :   0.22MPa

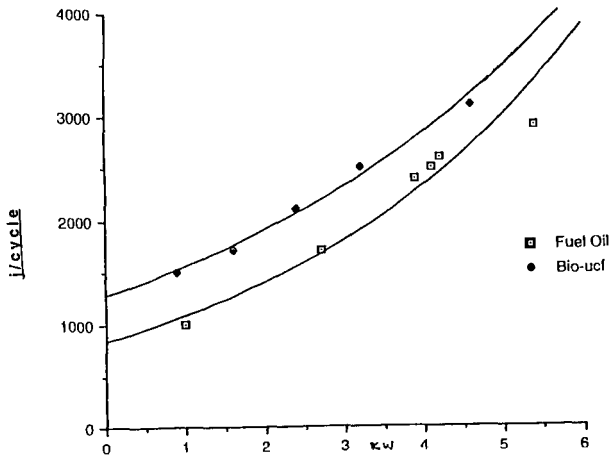Specimen results in comparison with Esso diesel 2000 fuel oil are given in Fig 1.

Figure 1: Energy consumption as a function of delivery power

The present research utilises a 4-stroke, 2 cylinder 600cc Lister-Petter diesel engine.A Heenan Froude hydraulic dynamometer is connected to the engine, as are auxilliary data collection apparatus as shown diagrammatically in Fig. 2.

The fuel formulation under investigation are based upon rape seed oil , peanut oil or sugar beet extract oil. Three different types of charcoal are under test. Also three different surfactants have been evaluated.In each case performance is compared with that of standard Esso diesel 2000.

The data obtained are;

engine torque	exhaust temperature
fuel consumption	oil temperature
air consumption	coolant temperature
speed	air temperature

Exhaust emissions are continuously monitored for levels of CO_2,CO and HC's levels.
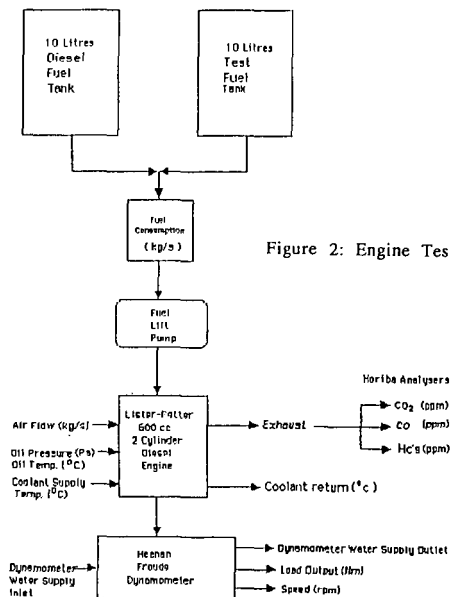

Figure 2: Engine Test Rig

Economics

The European Community's interest in bio-fuel arises in part from the Common Agriculture Policy (CAP).Farming at the present represents nearly 5% of the aggregrate Gross National Product of the EC member states and involves 9% of the workforce .Bio-mass crop production can contribute to this industrial activity and hence make a socio-economic contribution to rural development .Growing bio-mass will also avoid desertification of countryside. One tonne of crushed rapeseed produces about 320 kilograms of oil,and charcoal is readily available commercially.Additives are more expensive but are used only as 1%.It has been calculated that bio-ultracarbofluids will cost 21p per litre as compared to 12p for diesel , on the assumption that the rapeseed oil was grown on non-subsidised land .Hence preliminary estimates suggest that, with subsidies and economies of scale, the price of bio-ultra carbofluid could be comparable to diesel.

Conclusions

Results to date suggest that bio-ultrcarbofluids can be used in diesel engines without modifications. However the long term effects of corrosion, erosion and particle size on fuel handling systems require more detailed research using ASTM and EC test standards. The long term storage of the formulated fuels needs to be researched to see if this has any adverse effects such as oxidation of the oil components or settling of charcoal.

The EC is currently very keen to encourage the growing of energy crops since it will result in a reduction in the greenhouse gases, particularly CO_2 ,and reduce dependence on fuel imports. It would also encourage farmers to grow crops on set aside scheme.Hence there are good prospects for limited use of bio-ultracarbofluids.This would be greatly increased by direct or indirect state subsidies [9].

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THE THERMOCHEMICAL CONVERSION OF CELLULOSE TO OIL IN DIFFERENT SOLVENT-FEED RATIOS WITH DIFFERENT REDUCING GASES.

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Keywords: Liquefaction, Solvent, Cellulose, and Catalyst.

ABSTRACT

The conversion of cellulose (Solkaflock) with different aqueous feed ratio with 35 bar reducing gases (H_2 and CO) were studied in a batch autoclave system at 350°c in presence of 5% Pt/Al$_2$O$_3$ catalyst. Under these conditions, the conversion showed a general increase with increasing solvent/feed ratio, but more significantly when CO was used as the reducing gas. This is perhaps due to the better contact between the feed and catalyst as well as greater amount of solvent space. Decomposition of cellulose yielded mainly oil of relatively low oxygen content and high heating value. Increasing S/F ratio were produced lower amounts of oil and char but increasing the higher yields of water-soluble fractions. This is probably due to the higher liquefaction of gaseous products. Moreover, the oil were obtained from 10:1 (S/F ratio with H_2 gas) was contained 20.0% lights in comparison with 6:1 (S/F ratio with H_2 gas) contained 56.0% lights which is due to higher methanation reactions in 10:1 S/F ratio.

INTRODUCTION:

The effect of water to wood ratio has been found to be an important parameter during liquefaction with Na$_2$CO$_3$ and CO (1). In run 1, 2, 3, and 4, the effect of solvent /feed ratio, on the liquefaction of cellulose was studied using 5% Pt/Al$_2$O$_3$ catalyst in presence of CO and H_2 as reducing gases with water into fuels.

EXPERIMENTAL PROCEDURE:

These experimental works were conducted with 1-liter rocker stainless steel autoclave reactor. cellulose, catalyst and water were charged to it. Hydrogen or Carbon monoxide was added to the desired pressure (35 bar) and the autoclave was then brought to operating temperature at 350°c. and reaction time was 2 hours. After cooling the autoclave, the product gas was collected in a gas measurement system and were analyzed by GC. The aqueous phase was separated by decantation and the remaining oil and solids were removed by adding acetone, then were refluxed for 6 hours. Then filter it with filter paper by water vacuum. The residue is char and catalyst, was dried in an oven at 110°c for overnight. The filtrate was oil and acetone. The oil was recovered from acetone by rotaevaporation. These oil were further separated into lights, waxes by using solvent- heptane and then separated into asphaltene, resins,by using toluene. The feed, char, and oils were analyzed by elemental analyser.

## RESULTS AND DISCUSSIONS:

The reaction inputs, operating parameters and products distribution were shown in Table 1; and depicted graphically in Figure 1.

From the Table 3, the elemental analysis, it is seen that an increase in the H/C atomic ratio and a decrease in O/C atomic ratio as S/F changed from 6:1 to 10:1 in oils of runs 1 and 2 which indicate that increasing S/F ratio did not really promote the quality of oils.

The oil obtained from run 1 contained 56.0% light volatile whereas run 2 contained 20.0 %. Also, both Asphaltenes and resins of run 2 were greater in yields than those of run 1 which is

due to higher methanation ($CO + H_2$ -----> CH_4) reactions in run 2, that is more hydrogen consumed to form CH_4 not to hydrogenation with heavier fractions like Asphaltenes and resins.

However, in runs 3 and 4; both of which involved the use of CO as reducing gas. More lights 59.0% and smaller amounts of resins 17.2% and asphaltenes (11.5%) were produced relative to those of run 3; which probably the water-gas shift reaction was greater because of the greater volume of water present.

$CO + H_2O$ --------> $CO_2 + H_2$
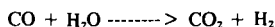
Therefore, the hydrogen is produced in situ which could have gained access to the sites and substrate molecules faster than the hydrogen present in the gaseous phase.

The calorific value of oil in run 1 is 7.840 Kcal/g (S/F ratio, 6:1) which is higher than that in run 2, 7.730 Kcal/g (S/F ratio, 10:1) when hydrogen is used as reducing gas. On the other hand, when CO is used as reducing gas, the calorific value of oil in run 4, (S/F ratio 10:1) is 8.530 Kcal/g is higher than that in run 3, (S/F ratio 6:1), 7.620 Kcal/g which is not likely as before. In both the cases, the increase in calorific value was probably due to higher yields of lighter materials in the oils and not to changes in S/F ratio.

The IR spectra and GC analysis of product gases in figure 3 and product gas distribution in table 5 is seen that run 3 and 4 were produced higher yields of CO_2 than run 1 & 2 because of predominance of the water-gas shift reaction in the CO atmosphere.

Run 2 produces higher yields of hydrocarbon gases which may probably the activity of the catalyst in hydrogen atmosphere.

In run 4, was produced low yield of hydrogen 3.14%, in comparison with run 3, 15.22%, may probably the reactivity of hydrogen produced in situ. If hydrogen was used up as postulated, then lower yields were expected.

The solvent water is a necessary component of the mixture undergoing the oil forming reaction. The source of water are as follows:

(a)   First, most substrates contain large amounts of moisture.

(b)   Second, since most organic wastes are highly oxygenated, water is formed merely by heating them to reaction temperature; so it is a reaction product.

(c)   Third, added to the reaction mixture as a solvent.

Moreover, Water acts as a solvent, vehicle and reactant. Solvation can occur between the hydroxyl groups of the substrate and water. It is an excellent medium for intermediate hydrolysis of cellulose and other high molecular-weight carbohydrates to water soluble sugars. The primary reactions in the conversion to oil likely involve formation of low molecular-weight, water soluble compounds such as glucose or pyruvic acid.

Water is a mechanical vehicle for facilitating mixing of reactants and preventing condensations to char by diluting the intermediates. Water acts as a reactant. The hydrogen added to the substrate comes from water, which consumes carbon monoxide by reacting with it to form carbon-di-oxide and hydrogen (Water gas shift reaction).

CONCLUSION:

1)   Lower S/F ratio resulted in greater yields of gaseous products, oil and chars. Higher S/F ratio resulted in greater yields of water solubles and water.

2)   O/C atomic ratio decreased with increase in S/F ratio.

3)   Changes in S/F ratio had no direct effect on the calorific values of the oils.

4)   Under CO atmosphere, when the S/F ratio was 6:1, the product of gases were contained a higher percentage of H_2 (15.22%) than S/F ratio 10:1 (3.14%).

5)   The high partial pressure of steam raises the operating pressure to levels where capital costs would be high.

6)   The heat required to bring water to the operating temperature and pressure adds considerably to the operating costs and

7)   The separation of the oil and water phases during the product recovery step is sometimes encumbered by emulsions.

8)   In case of tetralin, it can participate with the reaction at low temperature as well as low partial pressure raised; although water is more cheaper than tetralin.

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APPENDEX:

Table: 1   Reaction Inputs , Parameters and Product distribution

Run	1	2	3	4
Feed type (Solkaflock)	6:1	10:1	6:1	10:1
Feed (g)	40.0	40.8	40.0	40.8
Catalyst	5% PVAl$_2$O$_3$	5%PVAl$_2$O$_3$	5%PVAl$_2$O$_3$	5%PVAl$_2$O$_3$
Catalyst (g)	1.0	1.0	1.0	1.0
Suspension medium-water(g)	240.0	408.0	240.0	408.0
Reducing gas	H$_2$	H$_2$	CO	CO
Reducing gas (g)	2.09	1.6	29.34	22.40
TOTAL INPUT (g)	283.13	451.40	310.34	471.9
Temperature (°C)	350	350	350	350
Initial Pressure (atm.)	35	35	35	35
Heating up time (hr.)	2.2	2.0	2.0	2.0
Reaction time (hr.)	2.0	2.0	2.0	2.0
Max. Reaction Press. (atm.)	200.0	250.0	210.0	255.0
Final Reaction Press. (atm.)	22.0	18.0	35.0	40.0
TOTAL OUTPUT (g)	275.2	447.6	295.7	470.0
% Recovery from Autoclave	97.2	99.20	95.28	99.60
Product Distribution				
Gas recovered (g)	9.5	8.0	28.7	27.20
Water-soluble fraction (g)	3.3	12.0	4.5	14.0
Oil (g)	12.4	9.5	8.5	8.0
Char + Catalyst (g)	3.0	2.3	7.5	2.0
Water-recovered (g)	247.0	416.0	246.5	418.6
Water-Produced (g)	7.0	8.0	6.5	10.6
% Gas Produced (g)	18.42	15.68	16.50	12.5
% Water-soluble fraction	8.25	29.41	11.25	34.3
% Oil	31.0	23.28	21.25	19.60
% Char	5.0	3.18	18.25	2.40
% Water-Produced	17.5	19.60	16.25	26.47
% TOTAL RECEIVED	80.17	91.15	81.50	95.27
% CONVERSION	92.37	95.51	75.25	96.23

Table 2.   Product of gas recovery

Run	S/F* ratio	Conversion %	Initial gas (g)	Gaseous Product				
				Vol at S.T.P.	Mol. wt.	wt. (g)	Net wt.	% Prod'd
1	6:1	94.37	2.13	7.3	29.4	9.5	7.37	18.42
2	10:1	95.51	1.6	6.9	26.0	8.0	6.4	15.68
3	6:1	75.25	22.1	15.0	43.0	28.7	6.6	18.50
4	10:1	96.23	22.1	14.5	42.0	27.2	5.1	12.5

* Solvent/Feed ratio

Table no.　3. Elemental Analysis

Run	S/F ratio	Initial Press. (atm.)	Temp. (°C)	Feed Type	% Conversion	Feed stock					Char analysis					Oil analysis					H/C	O/C	Caloric value (Kcal/g)
						% C	% H	% N	% O*	% Ash	% C	% H	% N	% O*	% Ash	% C	% H	% N	% O*	% Ash			
1	6:1	35 (H₂)	350	Cellulose	92.37	41.5	6.1	ND	52.4	ND	63.3	5.7	0.2	30.0	0.8	72.1	6.9		19.7	NO	1.14	0.20	7 840
2	10:1	35 (H₂)	350	Cellulose	95.51	41.5	6.1	ND	52.4	ND	58.4	4.8	0.8	32.0	4.0	74.0	7.8		18.0	0.2	1.28	0.18	7.730
3	6:1	35 CO	350	Cellulose	75.25	41.5	6.1	ND	52.4	ND	63.2	4.0	0.3	25.0	7.5	73.2	7.2		18.5	0.5	1.17	0.19	7.620
4	10:1	35 CO	350	Cellulose	96.23	41.5	6.1	ND	52.4	ND	63.7	6.0		30.3		71.2	7.5		19.0	2.3	1.25	0.20	8.530

S/F ratio = Solvent/Feed ratio

* Estimated by difference

Table no.　4. Product oil composition

Run	Initial Press (atm.)	Temp. (°C)	Feed Type	Product oil composition				Elemental analysis										
								Heptane Soluble (boil)				Toluene soluble				Toluene insoluble			
				Heptane Soluble (%) Light volatiles	Heptane Soluble (boil) (%) (Waxes)	Toluene Soluble (%) (Asphaltenes)	Toluene Insoluble (%) (Resins)	% C	% H	% O	% Ash	% C	% H	% O	% Ash	% C	% H	% O	% Ash
1	35 H₂	350	Cellulose	56.0	14.5	17.2	12.3	82.2	7.5	10.3	ND	80.2	6.5	2.8	10.5	76.8	6.5	1.5	15.2
2	35 H₂	350	Cellulose	20.0	3.0	45.0	32.0	75.0	5.0	20.0	—	70.0	5.5	11.0	13.5	68.5	6.2	2.0	23.3
3	35 CO	350	Cellulose	46.4	7.5	28.3	17.8	79.7	7.8	12.0	0.5	70.7	7.9	19.0	2.4	78.0	5.8	16.0	0.2
4	35 CO	350	Cellulose	59.0	12.3	11.5	17.2	72.5	4.8	20.7	2.0	69.2	5.0	22.3	3.5	66.5	5.5	2.8	25.2

Table　5.　Product of gas distribution

Run	1	2	3	4
Temperature (°C)	350	350	350	350
Pressure (atm)	35	35	35 (CO)	35 (CO)
S/F ratio	6:1	10:1	6:1	10:1
Gas	H₂	H₂	CO	CO
% CO₂	28.83	17.70	58.16	71.12
%CO	48.14	25.22	24.51	22.86
%CH₄	0.082	1.58	0.91	2.14
% C₂H₆	0.039	0.53	0.25	0.60
%C₂H₄	0.044	0.05	0.28	0.0*
%C₃H₈	0.049	0.57	0.31	0.03
%C₃H₆	0.0124	0.01	0.08	0.01
% Butane	-	0.03	-	-
% Isobutylene	-	-	-	-
% 1-Butene	-	-	-	-
% Cis-2-butene	0.0233	0.07	0.12	0.03
% Trans-2-butene	0.0398	0.05	0.08	0.04
% Butadiene	0.0050	0.03	0.08	
% Total	77.27	45.84	84.78	96.86
% H₂+uP₂ *	22.72	54.16	15.22	3.14

* % H₂ + Unidentified Peaks were estimated by difference.

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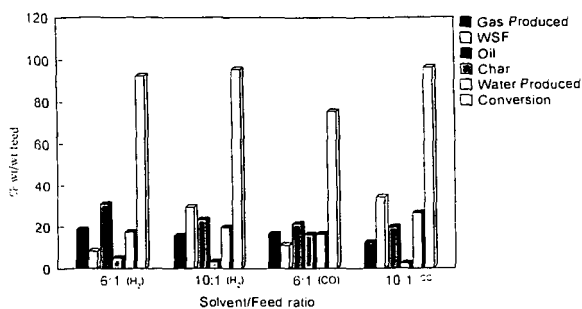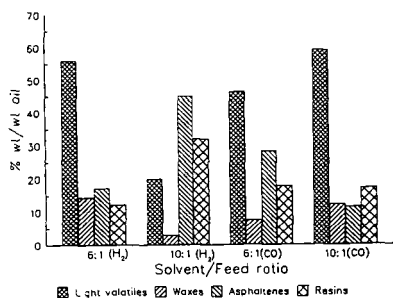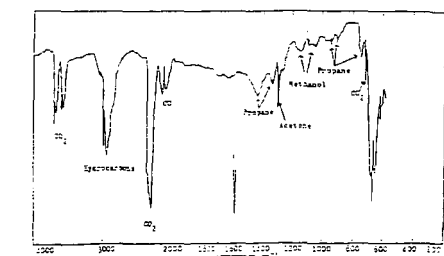Fig.　1.The effect of S/F ratio on H₂ and CO reducing atmosphere

Fig.　.2.The Effect of reducing gas on S/F on the Product oil Composition

Injected Sample = 18.0cmHg

Peak No.	Gas	RT(min)
1	CO	0.98
2	CO₂	2.45
3	CH₄	1.00
4	C₂H₆	1.55
5	C₂H₄	2.15
6	C₃H₈	2.75
7	C₃H₆	6.60
8	n-Butane	7.40
9	Cis-2-butene	12.45
10	Trans-2-butene	12.30
11	Butadiene	11.75
12	Unknown	
13	Unknown	

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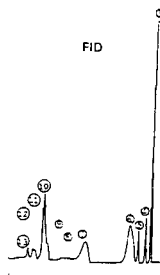
Fig. 3 : The IR spectrum and GLC chromatograms of the gaseous product from Run 1
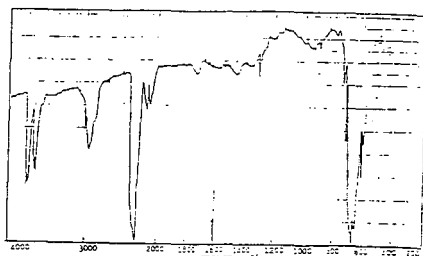
Injected Sample = 17.5cmHg

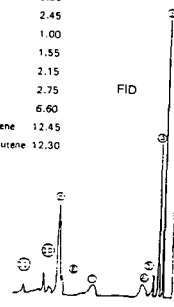| Peak No.	Gas	RT(min)
1	CO	0.98
2	CO₂	2.45
3	CH₄	1.00
4	C₂H₆	1.55
5	C₂H₄	2.15
6	C₃H₈	2.75
7	C₃H₆	6.60
8	Cis-2-butene	12.45
9	Trans-2-butene	12.30
10	Unknown	
11	Unknown	

KATH

FID

Fig. 4 : The IR spectrum and GLC chromatograms of the gaseous product from Run 4

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CELLULOSE DECOMPOSITION KINETICS - GLOBAL KINETICS FOR FUELS PROCESSING AND FIRE MODELING APPLICATIONS

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Keywords: Pyrolysis, Cellulose, Kinetics

Introduction

There has been an ongoing debate in the literature concerning the "true" global kinetics of cellulose pyrolysis. The global kinetics are of interest in modeling cellulose decomposition in many applications in which trying to represent the full complexity of the cellulose degradation process makes no sense. Roberts noted that the activation energy data on the pyrolysis of wood and related materials tended to cluster around two values, one at about 235 kJ/mol, and the other 125 kJ/mol [1]. Various reasons were advanced, including the possible role of catalysis and sample-size related issues. Lipska and coworkers reported values for cellulose near 176 kJ/mol [2, 3], while Shafizadeh reported 113 kJ/mol [4], although they concluded elsewhere [5] that the process can be divided into an initiation step (243 kJ/mol) followed by competitive pathways to volatiles (198 kJ/mol) and char (153 kJ/mol). Broido and Weinstein obtained 230 kJ/mol and an a pre-exponential of 5.25×10^{17} s^{-1}, using a TGA technique [6]. Meanwhile Lewellen et al. obtained a much lower activation energy of 140 kJ/mol, and a pre-exponential of 6.79×10^9 s^{-1} using a much higher heating rate [7]. Rogers and Ohlemiller obtained a similar value of activation energy, 163 kJ/mol, but at low heating rates, in a TGA [8]. Recently, Varhegyi et al. [9] obtained 234 kJ/mol and a pre-exponential of 3.9×10^{17} s^{-1}, also in a TGA system at low heating rates (10 K/min).

Thus there is not particularly good agreement as to the global kinetics of the process. The kinetics often appeared to depend upon the heating rate employed in the experiments used to deduce them. For our purposes, involving fire modeling, we were in a range of heating rates between those studied by many workers and we felt it necessary to establish more clearly what the applicable kinetics were. In addition to the question about Arrhenius parameters, there is also uncertainty concerning the order of reaction. While there is often a tendency to model the decomposition using first order decompositional kinetics, some careful studies clearly suggest fractional order kinetics are more appropriate. In this paper, we explore this subject using thermogravimetric analysis (TGA). We have also employed differential scanning calorimetry (DSC) to study the problem, and these results will be presented elsewhere.

Experimental

This work was carried out as part of a larger experimental program, concerned with the behavior of cellulosic materials under simulated fire conditions. Other results from this work have been reported previously[10]. The interest in the behavior of bulk solids under fire conditions dictated the general range of heating rates to be below 100 K/min, but we extended this to 1000 K/min for some experiments.

The pyrolysis behavior of purified cellulose in one case was studied in a standard TGA (DuPont Instruments Model 951). All TGA experiments were conducted in an inert gas environment (nitrogen). Temperature calibration of the TGA was of particular concern, since in this device the thermocouple was not in direct contact with the sample. The temperatures reported by the "standard" instrument thermocouple were observed to be significantly in error (over 20 K) depending upon how the experiments were performed (i.e., depending upon heating rate and amount of sample, gaseous environment). To obtain correct temperatures, an experimental protocol was adopted in which two identical experiments were performed, one in which a fine thermocouple was actually embedded in the sample powder. Using this procedure, we obtained much more satisfactory results, in terms of agreement with other careful work reported in the literature, as well as with our own DSC kinetics.

The cellulose used for all TGA work was a Whatman CF-11 fibrous cellulose powder that was used as-received. This cellulose is prepared from high purity cotton of 99% alpha cellulose content. The ash content is 0.009% by mass. The molecular weight of this material is in the range 36,000 to 45,000 daltons. The diameter of the fibres was 10 to 30 μm.

For some experiments, a heated wire mesh reactor was used, in order to achieve higher heating rates than are available from the TGA. This reactor consists of a thin wire gauze which is stretched between electrodes that provide current for resistively heating the gauze. The sample is held between two layers of gauze, and is uniformly heated. The apparatus is described in more detail elsewhere [11]. The samples used in this work consisted of either the same powders as used in the TGA work, or acid-washed filter paper (Munktell's OK/S2-80-200), with an ash content of 0.007%. The paper had a thickness of 168±8 μm, and was cut into rectangles approximately 1 x

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2cm. Since the powder and paper gave virtually identical results but had much different characteristic dimensions, this suggested that in-sample transport limitations were not important in this work, even at high heating rates. This will be further discussed below.

Results and Discussion

Figure 1 shows the results of experiments performed at high heating rates in the heated wire mesh reactor. Each datum represents the char residue yield (and thus one minus the total volatiles yield) from an isothermal experiment in which the sample is heated at the indicated rate to the abscissa temperature, and then allowed to cool at a rate of between 200 to 400 K/s. Mass loss during cooling is generally quite small compared to that during heating. The highest of the heating rates in Fig. 1 would be closer to the conditions that obtain in pulverized biomass combustion or pyrolysis, though still quite a bit lower. Nevertheless, there is good agreement with similar experiments performed at even higher heating rates [7,12]. The curves were calculated , assuming a typical moisture level of about 6%, from the parameters of [7], which were shown to apply to heating rates of 400 to 10,000 K/s.Thus the range for these global parameters is seen to now extend from about 1.7 K/s (100 K/min) to 10,000 K/s. As we have previously reported [13], there is, however, difficulty in applying these kinetic parameters at 5 K/min, as Fig. 1 also clearly shows. There is a significant underprediction of volatiles release rates observed at these heating rates.

Cellulose decomposition data from many other low heating rate studies also cannot be fit by the high heating rate parameters. Generally, activation energies of over 200 kJ/mol have been required, as noted above. Since we were interested in fire safety applications that put us in between the high and low heating rate ranges, we carried out an examination of the kinetics in this zone. This work could be carried out using TGA techniques. Two different types of experiments were performed. One type employed the ordinary constant temperature ramping techniques common in TGA work, and the other involved experiments in which the temperature was ramped at a fixed rate up to a particular temperature, and then the sample was held isothermally. Typical results of the latter ("isothermal") experiments are seen in Figure 2. The data of Fig. 2 could be analyzed to obtain kinetic parameters for a particular constant level of conversion. This is important in a case in which the kinetics change with conversion. The Arrhenius expression for a general n-th order reaction is:

$$\frac{d\left(\frac{M-M_f}{M_0-M_f}\right)}{dt} = -\left(\frac{M-M_f}{M_0-M_f}\right)^n A \exp\left(-\frac{E_a}{RT}\right) \qquad (1)$$

where M is the mass of cellulose or char at any time, the subscripts 0 and f denote initial and final, A is the Arrhenius pre-exponential, E_a the activation energy, R the gas constant, T temperature and t time. By taking the natural logarithm of (1), and then taking the derivative with respect to reciprocal temperature, the activation energy is calculable independently of any assumptions of order, if the calculations are performed at constant conversion. There is an issue of what to use for M_f in this case, since char yield can be a function of experimental conditions. In our TGA work, the value did not vary particularly much from 10%, and in testing our parameters for sensitivity to the assumed value, the variation proved unimportant.

Results obtained from the above calculations, using isothermal data of the type in Fig.2, are shown in Table 1. It is observed that the values obtained at low heating rates (1 K/min) are different from those from high heating rate experiments, and that they do not depend upon conversion. The values cluster near many others reported in the literature for slow-heating experiments. The pre-exponential factors, A, may also be calculated if a reaction order of unity is assumed, and are also shown in Table 1. The values are too high to represent unimolecular decompositions, as has been noted by others as well. Clearly the decomposition process does not involve rate control by a single step, in this range of conditions. Also, for comparison, a "typical" pair of kinetic parameters derived by this approach are used to try to fit the data of Figure 1. While a fair fit may be claimed at 5 K/min and 100 K/min, a very poor fit is obtained to the 1000 K/min data. Clearly such parameters are not appropriate for high heating rate modeling.

Figure 3 shows the values of activation energy obtained from the type of experiments as shown in Fig.2, but involving heating at a rate of 60 K/min. Several features were very different from those observed at lower heating rates. First, the attempts at fitting the data with a single activation energy failed. Rather, it was found that there were two different activation energy regimes. It was decided on the basis of observed behavior to divide the results into two regimes, one above 600 K and the other below. The regime below 600 K was seen to be characterized by an activation energy (and associated pseudo-first-order pre-exponential) that was quite similar to those obtained in the slow heating experiments, and shown in Table 1. The higher temperature regime was found to be characterized by a non-constant activation energy, but the values of apparent activation energy seemed to bracket those of the high heating rate experiments. It should be recalled that since the method of fitting the data attempts to avoid questions of reaction order change, an apparent temperature dependence of mechanism is the most plausible reason for the shift.

It may be noted from Fig. 2 that the major part of the decomposition is completed below about 600 K in all cases. This lends support to the idea that there is a shift in mechanism that takes place above that temperature, since Fig. 2 gave no evidence of two distinct kinetic steps. The higher the

heating rate, the more quickly the transition temperature of 600 K is exceeded and the more the higher temperature mechanism would show itself. As heating rates become so high as to force most conversion to occur in the high temperature regime, the kinetics again begin to look more simple. Unfortunately, it has been historically the heating rate regime between 1 and 10 K/min that has been the most explored, and this has put investigators squarely between the high and low temperature regimes in many experiments. We believe that this has led to many apparently contradictory results being reported.

The more traditional heating-ramp experiments also supported the two-regime proposal. Typical data are shown in Figure 4. These data were obtained from different non-isothermal TGA results, by determining the actual mass loss rates at different heating rates for a constant value of conversion (60% in Figure 4). These mass loss rates are the tangents to the mass loss curve at any time. It is clear from Figure 4, there is a point that fits neither curve cleanly, at around 600 K. From the data obtained at low heating rate conditions (0.1 and 1 K/min), the activation energy is calculated to be between 205 and 252 kJ/mol, varying randomly with conversion. For the data obtained at high heating rates (15 and 60 K/min), the activation energy varies between 137 and 180 kJ/mol. Depending upon how the point near 600 K in Fig. 4 is "counted", considerably higher values of apparent activation energy could be obtained.

Some analyses have been performed to address the question of reaction order. Letting
$\phi = [(M-M_f)/(M_0-M_f)]$, then generally speaking for any arbitrary n-th order reaction at constant temperature:

$$d\phi/dt = - [A \exp (-E_a/RT)]\phi^n = - k \phi^n \qquad (2)$$

Integrating yields different expressions for different values of n:

$$\phi = - k_0 t + C_0 \qquad (3)$$

$$\ln (\phi) = - k_1 t + C_1 \qquad (4)$$

$$1/\phi = k_2 t + C_2 \qquad (5)$$

where the subscripts on the constants indicate the orders assumed. The results of the isothermal experiments were examined for order, using these expressions. For convenience, a function $f(M/M_0)$ is defined such that:

$$f(M/M_0) = (F-F_{min})/(F_{max}-F_{min}) \qquad (6)$$

where F represents the values of the left hand sides of (3), (4) and (5). The order may be determined from the data by examining which assumed order gives the best approximate fit to linear, per (3), (4) or (5). Figure 5 shows a typical result, for an experiment at 584 K, following heatup at 1 K/min. Clearly first order is the best approximation to the data after an initial period of zero order. This result obtained in most low temperature (< 600 K) cases, and is consistent with earlier results in the literature [2,14]. The results of the experiments at higher temperatures did not give as clearcut results, and appeared to imply second order reaction might be involved, perhaps consistent with another report of near second order behavior [15]. Clearly this topic warrants further study.

Finally, we consider the question of transport effects as possibly responsible for the apparent shift in kinetic parameters. We believe this to be unlikely for several reasons. First, considering the analysis by Hajaligol et al. [16], it appears that despite of the endothermic nature of the pyrolysis reactions involved, the particles examined here are too small to be subject to a heat transfer limitation. Further, it is difficult to rationalize why use of a single heating rate could result in the behavior seen in Fig. 3, if a heat transfer limitation were involved. Thus it seems quite unlikely that a heat transport limitation is the cause of the observed variation in kinetic parameters.

Conclusions

It appears as though the confusing state of the literature on global kinetics of cellulose pyrolysis has as its cause a previously unrecognized shift in mechanism near 600 K. Depending upon the heating rate used to examine the kinetics, different values can easily emerge. We believe that the low temperature regime is characterized by an activation energy around 224 kJ/mol and an order that seems to go from zero, early in the process, towards first. The high temperature regime is characterized by neither constant activation energy nor order, and the apparent activation energy is centered near 140 kJ/mol. Together with an assumption of first order, a value of activation energy around 140 kJ/mol is clearly the most reasonable for applications involving pulverized combustion or pyrolysis of small cellulose particles. For fire modeling applications, both kinetic regimes may be of interest.

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**Table 1. Kinetic Parameters for Cellulose Decomposition from Isothermal
Experiments with 1 K/min Heating**

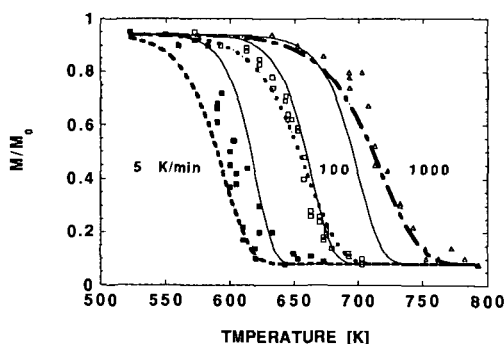| Remaining Mass (%)	E_a [kJ/mol]	A [1/s]
80	225	4.82×10^{16}
70	215	5.77×10^{15}
60	224	5.39×10^{16}
50	215	8.80×10^{15}
40	212	5.59×10^{15}
30	214	1.15×10^{16}
20	225	4.69×10^{16}

Figure 1. Comparison of char yield data obtained at indicated heating rates with model predictions. Broken lines are for kinetic parameters from [7], A= 6.79×10^9 s^{-1}, E_a = 140 kJ/mol. Solid lines are for A = 4.12×10^{16} s^{-1} and E_a = 224 kJ/mol.
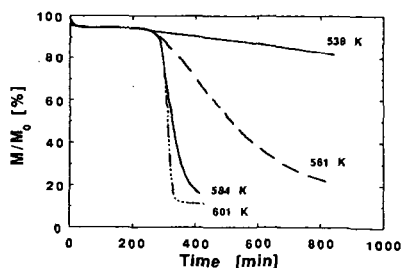

Figure 2. Typical isothermal experiment results, for 1 K/min heating to final temperature.
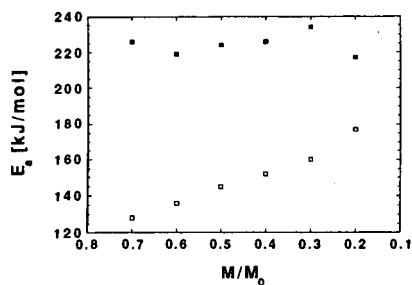
Figure 3. Activation energies obtained as a function of conversion in isothermal experiments involving heating at 60 K/min to final temperature. The open points are for results obtained for temperatures above 600 K and the solid points for temperatures below 600 K.
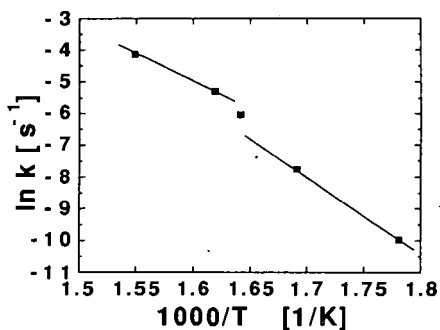

Figure 4. Arrhenius plot for $M/M_0 = 0.6$, from data obtained under nonisothermal conditions, at heating rates of 0.1, 1, 6, 15 and 60 K/min.
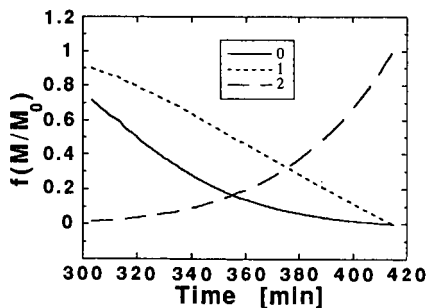

Figure 5. Test of different reaction orders on TGA data obtained in an isothermal experiment at 584 K.